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Corrosion inhibition of Copper in Nitric acid solutions by organic compound

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Abstract

The corrosion inhibition of copper by DES in 1MHNO_3 has been investigated by Weight Loss (WL), Temperature effect and electrochemical techniques such as Potentiodynamic polarization studies were used. Results showed that DES has good inhibition efficiency on the corrosion of copper in1M HNO_3 solution. Polarization measurement indicated that, the studied inhibitor act as a mixed type one. The inhibition efficiency depends on the concentration of inhibitor and reaches 99% at 30°c. The results obtained from the different methods are in good agreement. The SEM examination of the copper surface revealed that the compound prevented from corrosion by adsorption on its surfaces.

Keywords: *Nitric acid; Weight loss; corrosion inhibition; Scanning Electron Microscope(SEM); Electrochemical impedance spectroscopy (EIS).*

1. INTRODUCTION

Copper is extensively used in various industrial operations and the study of its corrosion inhibition is of importance, most investigations on the corrosion of copper have been carried out on. The development of corrosion inhibitor based on organic compounds has much scope in several industries because of their practical usefulness. The molecular structure of organic compounds used as inhibitor has been found to exert a major influence on the extent of inhibition of corrosion (Burleiqu etal. 1992; Lce etal. 1995;), copper and its alloys are widely used materials for their excellent electrical and thermal conductivities in many applications and recently in the manufacture of integrated circuits (Bork, 1988; Boger etal. 1972). The chemical dissolution and electro plating are the main processes used in the fabrication of electronic devices. The most widely used acid solution, so this medium has induced a great deal of research on copper [7-10]. Most of the effective organic inhibitor have hetero atoms containing multiple bonds in their molecules through which they can adsorb on the metal surface, In the present study organic sulphids as inhibitions for the corrosion of copper in 1M HNO_3 have been examined using weight loss measurement, Polarization studies and SEM process results are reported and discussed. The aim of the present investigation was to study the inhibitive action of organic compounds on the corrosion of copper in the 1M HNO_3 solution.

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2. MATERIALS & METHODS

Copper strips of size 4 X 1 X 0.25 cm and having the percentage comparison 99.5% of cu, 0.001 % of Ni, 0.019% of Mn, 0.116% of Si and balance impurities were used for electrochemical analysis, the copper samples were mechanically polished using different grades of emery sheets, washed with trichloroethylene and triply distilled water and dried.The organic sulphids used in this study were procured from Fluka AG , Switzerland, Analar grade HNO3 was used for preparing the aggressive solution.

2.1 Weight loss measurements

Weight loss measurement weight loss measurements were called out described in an earlier

work (Enteram A. Noor, 2009; Khaled etal, 2009; Schltze etal. 1987; Zarrouic etal. 2012) copper metal strip was immersed in 100m of inhibited and uninhibited solutions of 1MHNO3 for 2 hours. The inhibition efficiency was calculated from weight loss values obtained in the present and absence of the inhibitors at the end of definite intervals of time

$$\mathbf{I\ E\% = \{ (W_O - W_i) / W_O \}\ X\ 100}$$

Where

Wo = weight loss in plain acid

Wi = weight loss in inhibited acid

2.2 Temperatures Effects

The some procedure adopted for weight for studies at temperature of the study was varied from 35°c to 60°c. At the end of each experiment. The specimens were taken out washed both in running tap water and in distilled water. They were dried and their weights were measured. The loss in weight was calculated. Each experiment was duplicated to get good reproducibility . Weight loss measurement were performed in 1M HNO_3 with and without the addition of the inhibitor at their best inhibitory concentration percentages inhibitor at various temperature was calculated.

2.3 Polarization measurements

The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential was obtained. Both anodic and cathodic polarization curves were recorded by potentiodynamically using a corrosion measurement system consisting of a BAS Model 100 K H Z to 10MHZ a comprised elctrochemical analyzer (made in Lafeyette, in USA) PL-10 digital plotter (DMP -40 series the instruments,Division, Hovston, TX, USA) made by a platinum for and Hg/ Hg_2Cl_2 / 3M HNO_3 were used as he auxiliary electrode and reference electrode respectively. Which was controlled by a personal computer(Fiala etal. 2007).

2.4 EIS measurements

The electro chemical impedance spectroscopy were carried out using a transfer function analyzer, with a small amplitude . The double layer capacitance (C_{dl}) and the charge transfer resistance(R_t) were obtained using ac- impedance instrument (Benita Sherine etal. 2010; Quraishi etal. 2000;).

2.5 Scanning Electron Microscope

The copper immersed in blank and in the inhibitor solution for a period of 2 hours was removed, rinsed with double distilled water, dried and observed in a Scanning Electron Microscope to examine the surface morphology. The surface morphology measurements of the copper were examined using Hitachi S-3000 computer controlled Scanning Electron Microscope (Khiati etal. 2011).

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

The value of percentage inhibition efficiency (% I E), corrosion rate (CR) and surface coverage values (□) obtained from weight loss method at different concentrations of DES in 1M HNO_3 at 303k .The variation of inhibition efficiency with in increase in inhibitor concentrations is shown in Fig (2). It was observed that DES inhibits the corrosion of copper in HNO_3 solution at all concentrations used in study, i.e from l mM to 100mM maximum inhibition efficiency was shown at 100mM concentration of the inhibitor in $1MHNO_3$ at 303k. it is evident from Fig(2) that the corrosion rate is decreased on the addition of DES and also increase surface coverage.

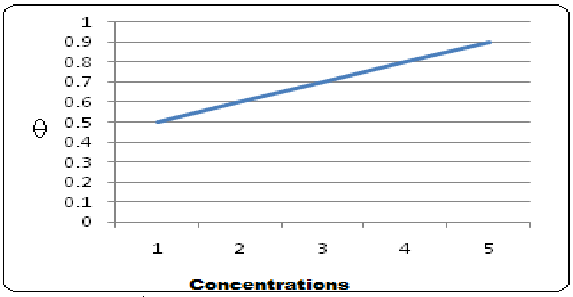

Fig. 1: Variation of inhibition efficiency on copper with different concentration of DES in 1MHNO3 at 30° C for 2 hrs

3.2 Temperatures Effects:

The value of inhibition efficiency obtained from weight loss measurement at the different temperatures of 303k to 333k in 1M HNO_3 solution at its best protecting concentration are presented in the Tables – 1. The inhibition efficiency decreased at high temperature.

Table 1. Corrosion parameters for copper in aqueous solution of 1MHNO3 in absence and presence of optimum concentration of DES at different temperature in 1M HNO3 for 2 hrs

Temperature (K)	Inhibitor	W (mg/cm2.h)	% I. E
303	Blank	0. 3932	-
	DES	0.0769	82.8
313	Blank	0.3124	--
	DES	0.0244	61.18
323	Blank	0.5723	--
	DES	0.0336	34.80
333	Blank	1.2031	--
	DES	0.5334	12.59

3.3 Potentiodynamic polarization measurement

Current – potential characteristics resulting from cathodic and anodic polarization curves of copper 1M HNO_3 in the presence and absence of DES at various concentrations are gives values of corrosion current (I_{corr}) corrosion potential (E_{corr}) anodic and cathodic Tafel slop (ba,bc) for DES at various concentration in 1M HNO_3.

In the case of polarization method the relation determines the inhibition efficiency (% I E) As it is shows in fig-(3) cathodic current – potential curves give rise to parallel Tafel lines indicating that the reaction is under activation controlled the cathodic current density decreases with the concentration of DES more over a small effect is observed on the anodic portions. This result indicates that DES is adsorbed on the metal surface on the cathodic sites and hence inhibition occurs, we remark that the inhibitor act on the anodic portion and the anodic current density is reduced.It seems also that the presence of the inhibitor the corrosion potential values in definite direction. These results indicated that DES act as a mixed type inhibitor.

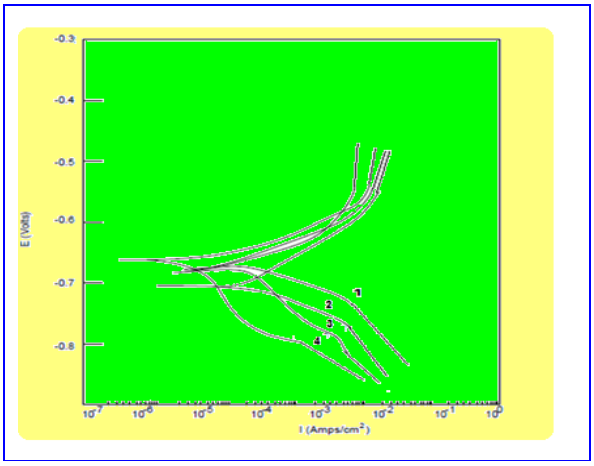

Fig. 2: Polarization curves obtained from potentiodynamic polarization studies for copper in aqueous solution of 1M HNO_3 in absence and presence of different concentration of DES.

3.4 Electrochemical Impedance spectroscopy

The results of impedance parameters (R_t and C_{dl}) for inhibitors are given in fig (4), the charge transfer resistance (R_t) value increase with increase in inhibitor concentrations but the value of durable layer capacitance (C_{dl}) decrease due to decrease in local dielectric constant and increase in thickness of the electrical double layer, suggesting that the inhibitor molecules function by adsorption at the metal solution interface. Hence the inhibition efficiency increases with increase in inhibitor concentration.
This may be due to the availability of more sites on the metal surface in 1MHNO$_3$ solution because of the lesser adsorption of the sulphide ions on the metal surface.

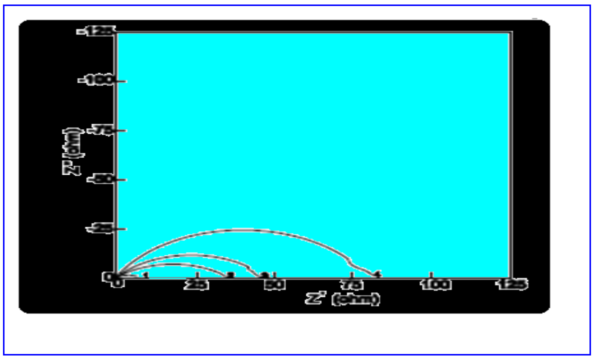

Fig. 3: Impedance diagram for corrosion of copper in 1M HNO_3 in absence and presence of different concentration of DES.

3.5 SEM analysis of metal surface

The SEM image of magnification (x 1000) of copper specimen immersed in 1M HNO_3 for 2 hours in the absence and presence of inhibitor system are shown in fig.5 (a,b).

The SEM micrographs of copper surface immersed in 1M HNO_3 in fig.5 (a) Shows the roughness of the metal surface which indicates the corrosion of copper in HNO_3. Fig.5(b) indicates that in the presence of DES, the surface coverage increases which inturn results in the formation of insoluble complex on the surface of the metal (DES inhibitor complex) and the surface is covered by a thin layer of inhibitor which effectively control the dissolution of copper.

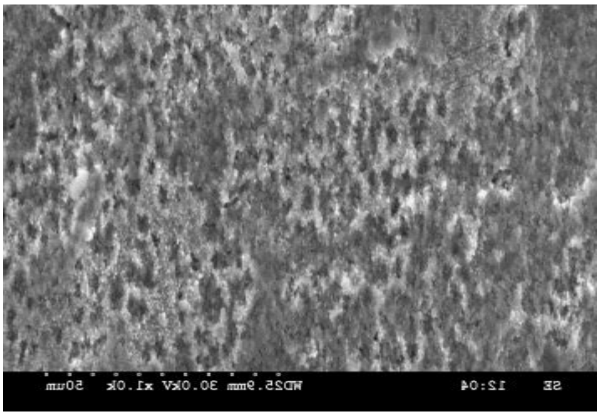

Fig. 4: (a) Pure copper metal + 1M HNO_3 Acid

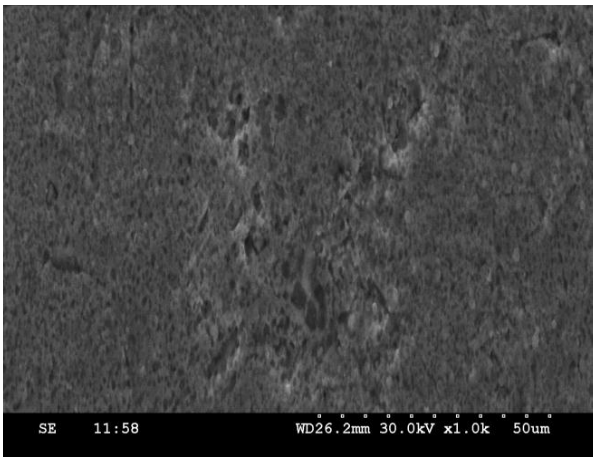

Fig. 4: (b) Pure copper metal + 1M HNO_3 Acid + Inhibitor (DES)

4. CONCLUSION

On the basis of the above results the following conclusion can be drawn.

- Results obtained from the experimental data shown that DES acts as an effective inhibitor for corrosion in 1MHNO_3acid
- The corrosion process was inhibited by adsorption of the organic matter on the copper surface. Inhibition efficiency increases with increase in the concentration of the DES but decrease with rise in temperature.
- Polarization measurements show that DES act essentially as a mixed type inhibitor
- The values impedance parameters justify the impressive performance of organic sulphide compound good corrosion inhibitor
- The SEM images confirm the formation of protective layer on the metal surface

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